

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : EDWIN ET AL. Confirmation No: 8773  
Appl. No. : 10/514,238  
Filed : JULY 25 2005  
Title : PROCESS FOR CARBON PRODUCTION

TC/A.U. : 1793  
Examiner : DANIEL C. MCCRACKEN

Docket No.: : EDWI3001/REF  
Customer No: : 23364

Declaration Under 37 CFR §1.132

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

Sir:

I, Emil Edwin, hereby declare as follows:

I have a Ph.D. from The University of Trondheim, The Norwegian Institute of Technology (1994), thesis entitled "Modeling, model-based control, and optimization of thermal cracking and ethylene production". Carbon formation from hydrocarbon gases was a key element in my Ph.D. work. and my experience in the field of catalysis comes from Research & Development projects and literature studies.

I am currently employed as a principal researcher for the Applicant company of the above mentioned application at the Research Centre, Rotvoll, Trondheim, Norway. I have worked in the field of hydrocarbon interaction with metals and oxides related to coke formation, metal dusting, carburization and CNF production for 14 years. I am author or co-author of five published scientific papers and am the inventor on at least 14 patent families.

I have read the Office Action of January 14, 2009 in respect of the above-identified application and the references cited and applied therein.

I make this declaration in support of the present application, and to provide evidence in rebuttal to the contentions set forth in the Office Action of 14 January 2009 that Rodriguez *et al.* (US 6,159,538, "Rodriguez") and Tennent *et al.* (US 5,165,909, "Tennent")

anticipate the claimed invention, or that Rodriguez and Tennent either together, alone or in combination with Schmidt (US 6,395,403, "Schmidt") render the claimed invention obvious.

The claims are novel over Rodriguez et al. and Tennent et al.

The Office Action states that Rodriguez and Tennent anticipate the process and products of the invention. However, neither document discloses porous transition metal catalysts for CNF production. In my opinion, the porous catalysts of the invention (e.g. Raney catalysts) are very different to traditional CNF catalysts and produce different fibrous carbon products.

Conventional catalytic production of CNF is understood to involve particulate catalysts in which the particles act as growth centres. The catalyst thus comprises active metal particles in pure or reacted form and of a size range comparable to the diameter of the carbon nanofibres eventually produced. If the particles are aggregated in clusters they can sinter into larger particles during catalyst reduction or during CNF growth.

De Jong *et al.*, Catal. Rev. - Sci. Eng. 42 (4) 481-510 (2000), cited in the present application, teaches that the catalytic form of the metals that have been used previously is bulk particles (size typical 100nm) or supported particles (10-50nm). Thus, the catalysts used in the prior art are active metals particles with typical particle size of 10 - 100nm.

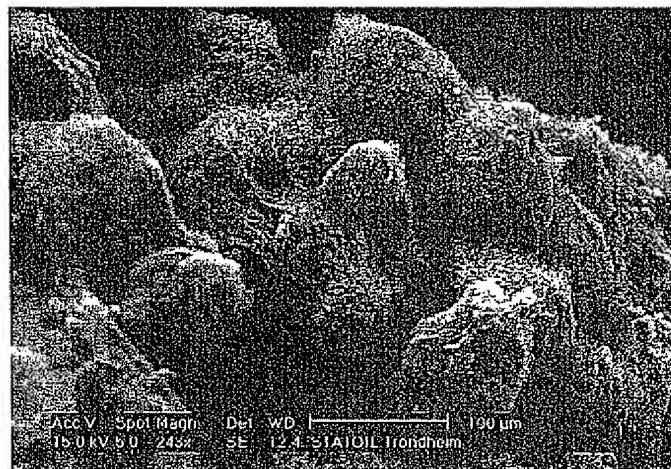
Also, Tennent teaches that the particles should be of reasonably uniform size and that they be isolated from each another, or at least held together in only weakly bonded aggregates (Tennent 8: 17-23), i.e. the size and particulate nature is important. Rodriguez contains similar teaching. For the particulate catalysts of the prior art, the thickness of the CNF fibres is dependent predominantly on the particle size of the catalyst metal.

On the contrary, the catalysts of the present invention are porous and their porous structure is made from a solid matrix, for example an intermetallic alloy where one component (e.g. aluminium) is removed, leaving a metallic skeleton with pores. It is the porous structure of the catalyst which affects the structure of the CNF products of the present invention.

As explained herein, we have found that the CNF fibres produced from porous catalysts have advantageous qualities with respect to fibre fraction, fibre density, degree of graphitic perfection, and amount of amorphous carbon on the fibre surface. The CNF produced according to the presently claimed invention therefore compares well to other commercial CNF products.

In the field of CNF production, process parameters are known to affect the nature of the resulting product. As noted above, the catalyst dimensions and surface characteristics affect the nature of the CNF product and therefore the CNF produced

using the highly efficient porous catalysts of the invention would be structurally different to those made using non-porous catalysts. As shown in figure 1 below, the CNF grows in nests in a dense manner surrounding the initial centre of growth (i.e. the porous metal surface). The highly efficient Raney catalyst produces a remarkably dense CNF growth pattern (figure 1 and 2). The prior art catalysts do not have the specified porous surfaces, therefore this pattern of growth would not be seen.



*Figure 1: Agglomerated nests of CNF produced with porous transition metal catalyst (AMPERKAT® SK-Ni5546).*

Moreover, because the porous metal used in the invention is a catalyst, it will not necessarily be used up in the CNF production process, i.e. the claimed CNF products will still contain porous metal catalyst (a feature which cannot be present in any of the prior art products because none of these were made with porous metal catalysts). One feature is that a catalytic metal skeleton layer can be leached onto an intermetallic construction alloy. As a result, CNF produced using porous metal catalysts according to the present invention will differ from CNF produced using other catalysts. The products of the invention are therefore novel in light of the prior art products by virtue of use of different catalysts.

SEM and TEM are generally recognised to be the most important tools for evaluating the amount of fibre, fibre structure and fibre diameter in the field of CNF. X-ray diffraction (XRD) is also used. Examples of SEM and TEM images of the Applicant's fibres can be seen in figures 2 and 3-4 respectively, which show CNF produced according to experiment 1, details of which are set out in the Annex.

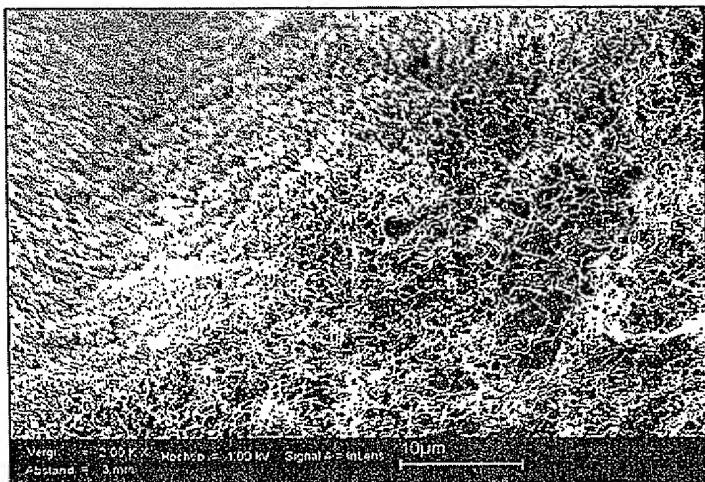


Figure 2. SEM "snap shot" of CNF produced according to experiment 1



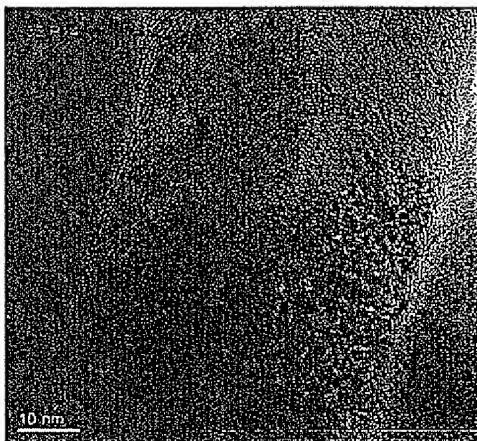
Figure 3. TEM picture of CNF produced according to experiment 1

The X-ray diffraction measurements set out in the following table show that the carbon fibres produced according to the invention have better graphitic perfection than the fibres commercially available from Pyrograf®. The  $d(002)$  value is used as a sign of graphitic perfection. Ideal graphite has a  $d(002)$  value of 3.335 Å thus, the closer the value is to 3.335 the higher is the graphitic perfection. It can be seen from the values below that the Applicant's fibres, produced with a porous transition metal catalyst, have better graphitic perfection than the Pyrograf® III commercially available fibres.

Sample No.	Origin	d(002) (Å)
1	Applicant	3.387
2	Applicant	3.396
3	Applicant	3.385
4	Applicant	3.376
P1	Pyrograf®	3.403
P2	Pyrograf®	3.407

*Table 1: XRD d(002) data on Pyrograf® III and Applicant's fibers*

Moreover, the CNF produced using the catalysts of the present invention (i.e. which has been pre-treated and grown in condition as described herein) also has low amounts of pyrolytic carbon phases on the fibre surface (i.e. the TEM picture below shows that the graphitic structure is seen all the way out to the fibre surface of CNF produced using a porous catalyst according to the invention according to experiment 1 in the attached Annex). Some end-uses of CNF require that pyrolytic carbon phases are removed in an extra process step. This extra processing is not required for the fibres of the present invention due to their low pyrolytic carbon content.



*Figure 4: TEM picture of fibre produced in experiment 1*

In summary:

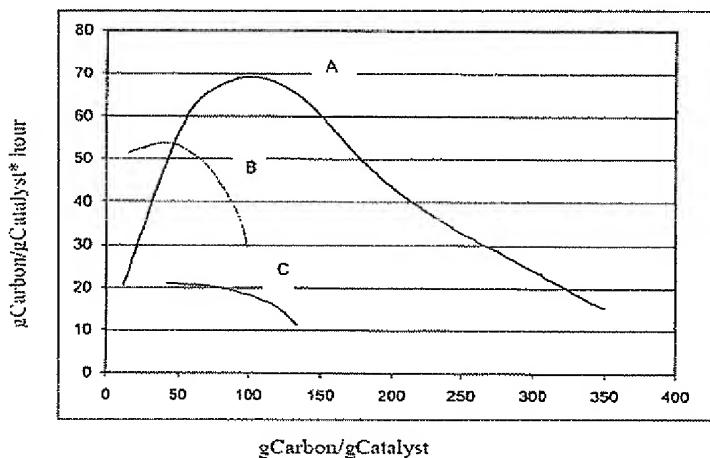
1. The porous catalyst produces CNF with a specific pattern of growth, dependent on the porous nature of the catalyst (see figure 1).
2. The CNF of the invention would be further distinguishable from the prior art products due to residual porous catalyst, i.e. the new method of production imparts

distinguishing characteristics on the product and thus the products are novel over the prior art.

3. The CNF produced using a porous catalyst has a higher degree of graphitic perfection than commercially available fibres (see table 1).
4. The CNF produced using a porous catalyst is shown in the TEM image of Figure 4 to have low amounts of pyrolytic phases on the fibre surface.

The claimed invention is not obvious in light of Rodriguez and/or Tennent  
The obviousness objections of the Office Action appear to be based on the assumption that the claims lack novelty over each of Rodriguez and Tennent. As discussed above, the feature of a porous transition metal catalyst is not disclosed in these documents and this renders the process and products novel over those known prior to the filing of the patent application.

The use of a porous catalyst in CNF production is not suggested in the prior art and thus is not considered to be obvious. We have surprisingly found that porous transition metal catalysts enable the production of a superior product (e.g., as previously discussed, high graphitic perfection, low amounts of pyrolytic phases) in a more efficient manner than the prior art methods. In order to further illustrate this, I submit the following figure as evidence of the advantages of the present invention.



*Figure 5: Catalyst efficiency (grams carbon produced per gram catalyst) against CNF mean formation rate (grams carbon per gram catalyst per hour)*

The above figure shows a plot of catalyst efficiency (grams carbon produced per gram catalyst) versus CNF mean formation rate (grams carbon per gram catalyst per hour) in which "A" shows the results for a porous Raney type catalyst according to the invention (see Annex) and "B" and "C" are data for non-porous nickel-containing

catalysts presented in Kuvshinov *et al.*, *Carbon*, Vol. 36, Nos. 1-2, p. 89 (1998) (copy attached). The Kuvshinov catalyst was the most efficient CNF catalyst based on methane feed we were able to find in literature at the time this experiment was performed.

The data in figure 5 is presented in this way because the catalyst cost is inversely proportional to catalyst efficiency (i.e. the more efficient the catalyst, the less catalyst is required) and the reactor size (cost) is inversely proportional to the mean formation rate if catalyst efficiency is fixed. Thus high catalyst efficiency and mean formation rates are advantageous in order to reduce catalyst and reactor cost. The curves marked B and C are prepared from the results shown in figure 2 in the Kuvshinov *et. al.* paper which shows the time dependency of carbon formation rates.

The curve marked A prepared from the results shown as "A" in Figure 6 below. Carbon deposition is the integral of the curve and mean production rate is the calculated carbon deposition divided by the production time (excluding the pre-treatment time).

The Kuvshinov catalyst, which produced plots B and C of Figure 5, contained 88 wt % Ni and was prepared by joint precipitation of nickel and aluminium hydroxides from a mixture of their salt solutions. The sediments were filtered, washed, dried at 120°C and decomposed in nitrogen at 350°C. Then the samples were reduced in hydrogen at 550°C for 3 hours. The CNF was grown on 0.002 g catalyst in high purity methane (99.99% CH<sub>4</sub> and H<sub>2</sub>) in a vibrofluidized bed at 550°C and 570°C. The Kuvshinov paper shows that lowest CNF yield and highest mean deposition rate is experienced at the higher temperature. Atmospheric pressure is assumed.

Experiment A in Figure 5 was carried out using 0.043g porous Raney catalyst; (Commercial name: AMPERKAT® SK-Ni5546 from H.C. Starck) which comprises 92-96% Ni and 4 -7.5 wt% Al. The catalyst was inserted into a fixed bed reactor, and then the bed was heated in an H<sub>2</sub> atmosphere until the temperature reached approximately 480°C, at which point the gas was changed to 1.6L/min pure methane for a 30 minute pre-treatment period producing 2-5vol%H<sub>2</sub> in the effluent gas. This indicates that some CNF is also produced during pre-treatment, however the rearrangement of the catalyst surface during pre-treatment is also associated with some carbon uptake and saturation of Nickel matrix. After pretreatment the temperature was raised to 630°C and then 12.5 vol% H<sub>2</sub> was added to the feed gas. Thus the H<sub>2</sub> fraction was always higher than 12.5 vol% and peak reactor effluent concentration was approximately 30 vol% H<sub>2</sub> due to methane cracking. Total pressure was 5 bar.

Although the reactor and process conditions used in Experiment A of the present invention and Comparative Experiments B &C of Figure 5 are not identical, both experiments focus on high carbon yields and thus I believe that in each case the process conditions are optimised for the catalyst system used. In fact, the reactor conditions are regarded to be better for the Kuvshinov experiment, therefore the fact

that the method of the invention (as illustrated by plot A in Figure 5) give better results is even more surprising.

It is clear from the above plots that the porous skeleton catalyst according to the present invention shows a remarkable improvement in efficiency compared to dedicated highly efficient CNF catalyst (i.e. arguably the most efficient prior art catalyst). This surprising advantage is considered further evidence of non-obviousness.

The claims are not obvious in light of Rodriguez and Schmidt or Tennent and Schmidt

The Office Action states that, as a porous Raney-type catalyst is disclosed in the Schmidt citation, the skilled person looking for an alternative catalyst for CNF production would be motivated to use the porous catalysts of Schmidt.

There is no suggestion in Schmidt that the catalysts could be used for CNF production. Schmidt is concerned with porous base metal catalysts which have at least one precious transition metal dopant distributed on the surface and teaches the use of such catalysts in hydrogenation reactions. In contrast, the present invention is concerned with dehydrogenation. I see no reason why someone seeking a catalyst for dehydrogenation would look to a document which describes catalysts for doing the exact opposite. I do not believe that it is obvious to use a hydrogenation catalyst for dehydrogenation.

The patent application notes that the use of porous catalyst has the further advantage of allowing the use of natural gas without requiring purification (page 5, final paragraph). It is also noted in the application that CNF yield is significantly enhanced by the use of a porous transition metal catalyst (page 2, lines 7 to 9, page 3, lines 29 to 36).

It cannot be obvious from the prior art documents, which teach particulate catalysts or catalysts for completely different processes to the CNF production of the present invention, to use a porous metal catalyst for the production of CNF fibres. A further advantage of the porous skeleton catalysts of the invention is that they can conveniently produce high amounts of CNF, particularly if subjected to a pre-treatment phase. This pre-treatment is described on page 12 of the application as filed (see lines 16 onwards). The catalyst should be treated with a gas with reduced hydrogen content and at a lower temperature than the CNF production temperature for a limited time, prior to the main CNF production stage.

Figure 6 below shows carbon deposition as a function of time for experiment A (previously discussed) and Experiments 5 and 6 outlined in the Annex. Experiments 5 and 6 used 8NI/min pure CH<sub>4</sub> in a rotating reactor and identical catalysts. They involve a small temperature difference and a difference in catalyst amount, however neither of these features could be responsible for the marked difference in carbon

production rate. Experiment 5 used a catalyst pre-treatment step as described in the present invention and Experiment 6 did not.

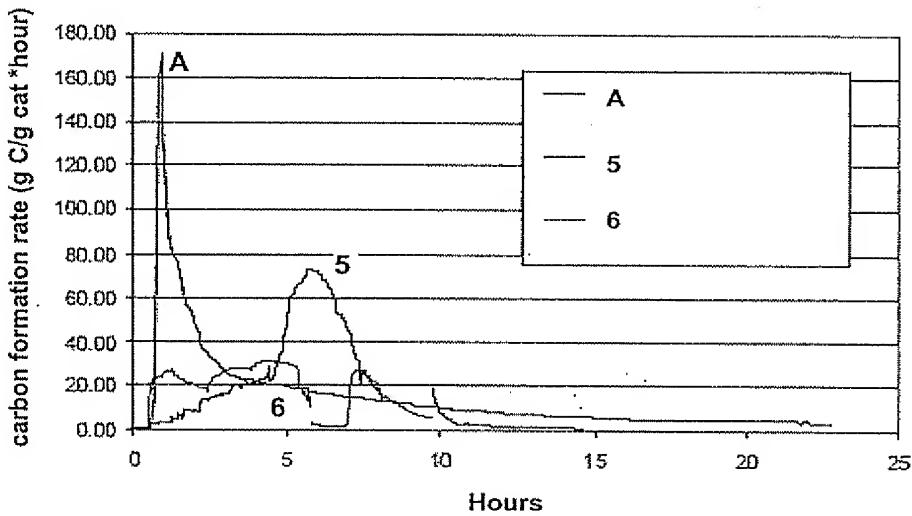


Figure 6: Time dependent carbon deposition. Experiment A used a fixed bed reactor, 5 and 6 are from rotating reactor. Curve 5 is with pre-treatment and 6 without pre-treatment.

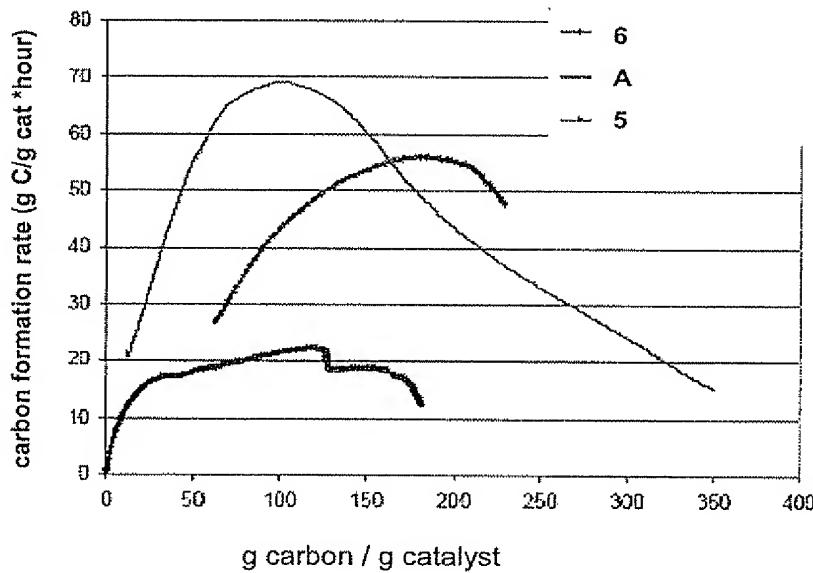


Figure 7: Rotating reactor experiments 5 and 6 compared to fixed bed experiment A. Curve A is fixed bed experiment A, curve 5 is larger rotating reactor experiment with pre-treatment and curve 6 is larger rotating reactor experiment without pre-treatment.

The effect of pre-treatment on carbon yield is shown further in figure 7. This experiment also shows that the good carbon yield found in the experiments with small amounts of catalyst (e.g. experiment A) is not related to experimental scaling effects.

The catalyst pre-treatment according to the present invention thus results in the catalyst producing unexpectedly high amounts of CNF per gram of catalyst at a unexpectedly high mean production rate (gCarbon/gCatalyst\*hour) (figure 7). As noted above, I believe that the porous catalysts are suited to high production rates of CNF due to the special catalyst surface characteristics found in the porous metals used (see the patent application, page 3, lines 29 to 36).

We have also found that CNF production using the porous catalysts of the invention can be made more efficient by increasing the pressure of the reaction. Taking the integral of the curves in figure 8 shows an increase in yield from 7 grams of carbon per gram of catalyst to 86 grams of carbon per gram of catalyst when pressure is increased from 1 bar (blue plot) to 5 bar (pink plot).

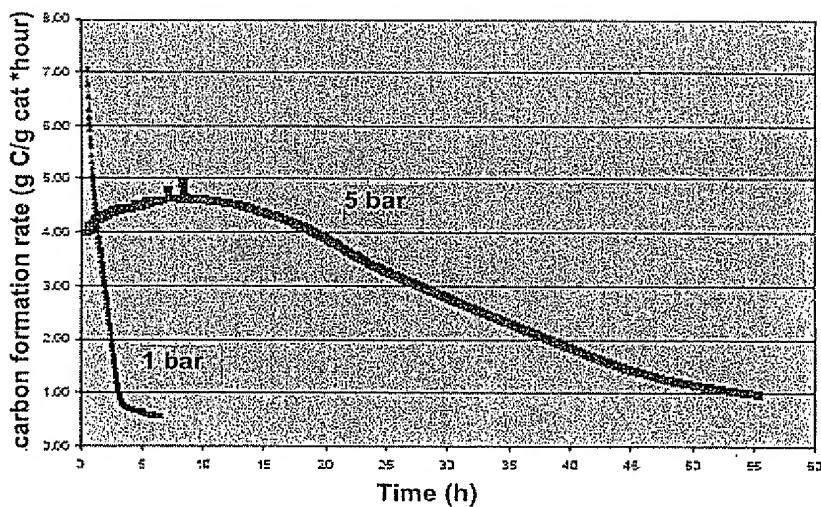


Figure 8. Carbon deposition as a function of time (effect of pressure)

In summary, use of porous catalysts in CNF production gives high yields of CNF with desirable characteristics. The process of the invention allows further improvements by using the pre-treatment step described in the application and/or increased pressure.

In view of the above, the use of a porous skeleton metal catalyst in the production of CNF is therefore considered a novel and inventive process giving rise to novel and inventive products.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine, or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the above-captioned patent.

By: Emil Ed  
EMIL EDWIN

Date: 30/9 - 09

Annex - Summary of Applicant's Samples and Experimental Conditions

Sample No.	T (°C)	Pretreatment T (°C)	P (bar)	Catalyst amount (mg)	Hydrogen fraction (start/end of run)	Deposited carbon (gC/gcat)
A	630	480	5	43	30%/12.5%	350
1	680	480	5	118	(c.t.eq / 25 vol %)	140
2	680	480	5	119	(c.t.eq / 40 vol %)	94
3	680	480	5	119	(c.t.eq / 10 vol %)	190
4	630	480	5	115	(c.t.eq / 25 vol %)	193
5	650	480	6	490	< 25%	230 catalyst not deactive
6	630	-	6	390	-	

All of the above were carried out using AMPERKAT® SK-Ni5546 catalyst.